FUEL CELLS

Recent Advances and Market Potential

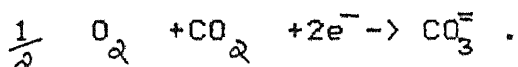# 5. MOLTEN CARBONATE FUEL CELLS

The MCFCs operating at a temperature mcv 650 C has been under intensive development for the last decade as a second generation FC. The melt chemistry and electrochemistry involved in the MCFC are unique. At the anode of the MCFC, the net reaction is

$$H_2 + CO_3^= \rightarrow H_2O + CO_2 + 2e^-,$$
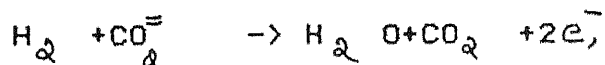
whereas at the cathode

$$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^= .$$

is the net process. The CO has a function similar to Lewis acids (for example, the proton) in low-temperature cells such as the PAFC; however, protons are transferred by another shuttle mechanism. An important attraction of the MCFC is the simpler overall plant design made possible by its ability to accept CO and CO_2 as well as H_2; for this reason, a lower first cost of the overall MCFC plant is projected than for the PAFC, while still retaining high efficiency. The other inherent advantage of the MCFC is its favorable ratio of high-quality heat (above 55° C) to total energy.

5.1 Commercialisation.

The MCFC, following a very intensive development effort during the last eight years, may now be about 7 to 9 years behind PAFCs from commercialization, depending on the particular application involved. It appears to have a useful future in the industrial congeneration market. Since it is a dc device, it may be particularly suitable for use with electrochemical processes, for example, in the chlorine-caustic and aluminum industries. In the former, it has the additional advantage of being usable for efficient consumption of any H_2 produced in the process along with some clean fossil fuel (NG or syngas from coal). For the industrial application, a heat-rate of about 8000 BTU/kWh may be most desirable, which will produce about 3500 BTU/kWh of steam. The major advantage of the MCFC over acid cell is that it can use internal reforming i.e its waste heat is directly available within the cell for the conversion of disulphurised methane directly to H_2 in a driven reforming reaction in the cell anode chamber. In the internal reforming type of cells (IRMCFC), the space velocities are relatively low and reforming rates are quite adequate, provided that the reforming catalyst is protected from catalyst poisons (particularly Sulphur and traces of carbonate).

The IRMCFC promises to have a very bright future for both electric utility and on-site applications, using NG, provided that the installed cost is economically competitive. Installed-cost estimates are at present in the $1200-1300 kW range. The higher fuel efficiency would certainly make the IRMCFC somewhat more attractive economically than the PAFC. If it is commercially available, it might therefore be preferred by the utility over a PAFC offered at the same price. However, this scenario implies that the PAFC could be made obsolete by the

MCFC, which is unlikely to happen in view of the difference in the periods of commercial introduction between the two systems: the PAFC should be well down the learning curve and probably available at less than $ 1000/kW installed when the IRMCFC goes into pilot production.

The consensus in the utility industry seems to be therefore that the PAFC and the IRMCFC will both find their place in the generation mix. The PAFC will be introduced earlier and will fill the lower efficiency end of the market (8000 BTU/kWh).

Because of its early introduction, its production cost will be relatively mature when a premium cost IRMCFC is first introduced to fill the higher-efficiency market. Finally, the market for the PAFC may eventually be limited by Pt supply. The favourable ratio of high-quality heat to total energy may open up a significant market for stand-alone applications, with the possibility of internal reforming of natural gas followed by early commercialization of MCFCs operated at atmospheric pressure and at a wide range of sites.

5.2 Research Priorities

There still remain several technical difficulties that must be resolved before successful commercialization can start. These relate to improved endurance and performance. As regards the former, small amounts of electrolyte are lost from cells and stacks by corrosion and vaporization. The present stability of electrodes is not adequate for 40,000 h of operation under pressure; however, their stability under non-pressurized operation may be satisfactory for periods approaching this goal. Long-term creep under compressive stress and corrosion of non-electrode cell and stack parts are matters of continuing concern. Long range research is needed to understand the mechanisms of corrosion reactions. If the operating temperature could be lowered, cell endurance would be greatly improved (especially if it is limited by corrosion), even though overall performance would be somewhat less than at 650° C.

Electrode performance, though adequate at present, can be further improved by optimization of electrolyte composition. Significant improvement in performance and lower first-costs would perhaps be possible if direct HC oxidation could be achieved. The effect of Sulphur and other contaminants puts significant limitations on feed-gas quality. Improving the cell tolerance to contaminants would reduce the costs of cell clean-up and simplify the overall system. Another significant area of investigation is the probable quantitative effects of various structural and operating conditions on performance decay.

Fundamental research on ceramic and solid-state science may be needed to support the development of a conductive ceramic that may be used either as an MCFC electrode substrate or as a solid electrolyte usable at temperatures between 500 and 650° C.

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Research requirements include the development of alternative cathode materials with special reference to the interpretation of experimental results and the development of predictive theory pertaining to conducting ceramics as cathode materials. Elucidation of electrode kinetics is of prime importance and studies of reaction mechanisms and transport in the electrolyte, as a function of electrolyte composition (not limited to alkali carbonates), temperature, and electrode material etc. are also important. Further elucidation of corrosion mechanisms under represnetative three-phase (molten salt-solid-gas) contacts and polarization conditions, as well as modelling of corrosion rates is also required.

Another important area for development is the design of a direct HC electrode and understanding of the kinetic issues involved in the operation of this device. Similarly development is needed of sulphur- and HCl-tolerant electrodes, in conjunction with a sulphur- and chloride-rejecting electrolyte. The kinetic issues involved in understanding the operation of this electrode should be clarified.

Equally significant are fundamental physicochemical and engineering studies on the determination and theoretical prediction of gas and solid solubilities, gas and ionic transport properties, capillary behavior of the molten electrolyte as a function of composition and temperature etc. Of particular significance is the development of novel performance and performance-decay models, in conjunction with experimental data to verify model validity. Further, development of in situ diagnostic techniques is needed for applications to cells and cell stacks.

6. SOLID OXIDE FUEL CELLS

The solid oxide fuel cell (SOFC) has a moderately long history, with an early significant development effort emerging in industrial research laboratories in the mid-to-late 1950s. The development continued for 20-25 years at a low level. During the last five years, this effort has been expanded considerably. Currently SOFCs are at the demonstration stage for useful cell performance and endurance with a geometrically simple cell design. The present program calls for deployment of small laboratory demonstration test-units at selected, technically sophistacated customers. Other R&D efforts are also in progress. A particularly noteworthy development effort is focused on a monolithic cell design at the Argonne National Laboratory (ANL). This design is aimed at very high specific power and power density.

SOFCs have several characteristics that are distinct from those of other FCs. Chief among these is operation at a temperature around 1000°C. This feature allows electrochemical oxidation of H_2 and CO without an added specific catalyst. Fuel versatility is a significant advantage in the use of SOFCs for some applications. The SOFC also offers the possibility of operating

at higher power densities. The components of the SOFC are primarily ceramics. Although relatively cheap materials are used, the processing techniques needed to fabricate the final, composite article are very difficult to implement. Recent advances in processing techniques are viewed as major steps in advancing SOFC technology toward commercialization.

6.1 Commercial Status

A series of technical accomplishments in the recent years have led to improved materials and processing that have resulted in stable cell performance at high power density. It now appears that this technology with an aggressive development effort can reach commercial status by about 1990. If this goal is met, SOFGs will be of value to a broad segment of the U.S. economy 10 to 15 years earlier than was believed to be the case earlier.

Westinghouse Electric (WE) is the only U.S. manufacturer pursuing the commercial production of SOFCs. The WE focuses a significant potential for combined heat and electric power plants for the industrial and commercial markets and aims to penetrate the market by 1990.

6.2 R&D Priorities

The single most important need for research support falls in the area of ceramic science and involves finding improved materials and processing methods.Work on improved ceramics should focus on two main aspects : (a) macrostructure, where there is a need to develop processes suitable for use with new components and novel cell geometries, and (b) microstructures, where there is a need to understand atomic-scale processes, which will allow creative engineering of cell components with desired pore structures or the use and/or control of sintering processes to prolong macrostructural stability. Other issues in this category include fundamental studies of multicomponent diffusion with various driving forces, segregation of impurities at grain boundaries, and solid/solid-surface interactions. Research on ceramic science is expected to have a significant and early impact on SOFC development. An important objective is advancing basic knowledge of the relation between ionic conductivity in solid oxides and their structures, with the goal of greatly increasing the number and range of substrates that may be used in SOFCs at temperatures even higher than those now employed.

As regards materials it is necessary to perform studies of new materials for cell components in order to ensure technology improvements. Research in this category includes studies of the electronic and ionic properties of oxygen-conducting electrolytes, and would include both contemporary and new electrolyte compositions. The effects of impurities, of the type that might arrive at the electrolyte by diffusion from the electrodes, should be considered. Similarly, studies are needed on the properties of new candidate materials for use as the anode, cathode, or interconnection.

For the purpose of obtaining novel and improved cell designs, computer models for the SOFC stack will have to be developed. Important components of the model include kinetic processes at reaction sites, electrochemical mechanisms, and modelling of overall system performance. Models, when verified by critical measurements, provide insight and a useful design tool. Also required are detailed studies concerned with the design and optimization of electrode microstructures, from the point of view of heat transfer and kinetics. An integrated SOFC model is expected to be useful for these studies.

The chemical behavior of cell components, under various cell environments, can often be understood in terms of thermodynamic analysis. However, some of the important required thermodynamic data for the complex phases are not known and need to be measured. Because the cell consists of layers of ceramic materials in intimate contact, it is inevitable that stresses will arise as the result of differential thermal expansion. Non destructive techniques to measure these stresses in cells are needed, not only for quality control during production but also as research tool aiding in compatibility evaluations for new materials.

7. INTERDISCIPLINARY RESEARCH

The above discussion shows recurring emphasis on such topics as materials research and electrochemistry, although the particular problem areas within a given disciplinary field tend to be distinct for each FC type. Nevertheless, it is instructive to categorize the preferences for studies in interdisciplinary research areas that result from examination of research needs for each type of FC. The results of basic studies in the indicated interdisciplinary research areas should ultimately benefit all FC developments. At present, nine primary interdisciplinary research areas have been indentified by the AFCWG. These include: (1) fundamental electrochemistry, including interfacial structures, electrocatalysis, electrode kinetics, and electrode properties; (2) new materials and processes, including new catalysts, electrolytes and electrodes, as well as new procedures for the preparation of fuel-cell components; (3) degradation, including studies of mechanisms and processes that limit cell life; (4) transport properties such as solid-, liquid- and gas- phase conductivities, diffusivities, viscosities, thermal conduct-ivities, transport numbers, solid-state mobilities, and the development of new methods for determining these properties; (5) surface science defined as studies of surface phenomena, metal-ceramic bonding, surface-energy changes at electrodes, structure and morphology of interfaces; (6) applications and development of new diagnostic techniques in order to gain improved understanding of fuel-cell behavior by performing experimental measurements, including verification of fuel-cell models; (7) thermochemistry of materials such as studies of phase equilibria, solubilities, and solution behavior; (8) studies of electrode microstructure, including theoretical investigations of porous electrodes and utilization of the results of these investigations in the design and performance evaluation of fuel-cell electrodes; (9) novel cell concepts such as new approaches to the configuration of cell structures and their evaluations.

The immediate motivation for research support in the areas listed above is based on their perceived importance in contributing, over the long-term, to the successful commercialization of improved cells. The relative distributions serve to emphasize the evident preferred need for research on new materials and processes, studies of electrode microstructure, novel cell concepts, corrosion, and fundamental electrochemistry. Relatively high funding levels are required either because of recognized long-term merit for the research or because of the need for substantial funding in order to obtain a proper assessment of long-term merit. In general there is a clear preference for basic investigations in electrochemistry, electrode microstructure, corrosion, and surface science for the low-temperature cells (PAFCs, AFCs, SPEECs), whereas funding-level recommendations tend to be more uniformly distributed in all areas in support of the high-temperature cells (MCFCs and SOFCs).

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About this Document

The US Department of Energy had set up an Advanced Fuel Cell Working Group (AFCWG) for a scientific evaluation of the current status of fuel cells with special emphasis on the indentification of long range research areas that may be required for future commercialisation. The AFCWG has subsequently identified certain priority research areas that should be persued over the long term in order to advance the design and performance of fuel cells of all types. The highlights of the findings and recommendations of the AFCWG were reported in a set of six review papers appeared in early 1986. The present document is a summary of these papers for information and wider dissemination.

C O N T E N T S

1. INTRODUCTION.

Fuel cells offer a very attractive device for reducing the amount of energy required to produce a specific amount of electricity. The use of FCs further offers the potential of lowering the cost of electricity. Reducing required energy inputs and lowering the cost of electricity are related but separate, important issues. Reducing the required energy inputs decreases the need for energy imports and also the amount of domestic GNP required for new energy production or utilization. These advantages, in turn, improve the balance of payments and free resources for other uses. Reducing the cost of electricity will further benefit consumers and their utility suppliers.

The potential benefits of Fuel Cells (FC) development and use are the result of unique FC properties. The FC is an electrochemical device which produces electricity directly from the galvanic oxidation (combustion) of a fuel. The usual steps involving primary conversions to heat and mechanical energy are omitted in FCs. The theoretical FC efficiencies are not limited by the Carnot cycle and may be very high. Actually achieved efficiencies in electricity production with FCs exceed those of conventional methods for power generation. For example, FCs using natural gas today produce electrical energy at a conversion efficiency of 40% and will in the future have efficiencies up to 65%. Coal-fuelled FC systems with comparable FC technology are expected to reach the 35 to 60% efficiency range in the near future. The current U.S. averagae for electric power generation is about 33%. For a new system, a doubling of fuel efficiency will reduce the required primary energy inputs correspondingly, whether imported or domestic fuel supplies are used.

A second important characteristic of the FC is the relative independence of power-plant efficiency on power-plant size. Thus, a 500-kW(e) power plant may have the same efficiency as a 500-MW(e) power plant. This fact has a tremendous impact on utility purchase of FCs. In the sixties and seventies, electric utilities in the U.S. and elsewhere began to purchase power-plant units of very large size. One thousand MW(e) coal and nuclear plants were designed and built or almost built. Unfortunately, nuclear power plants in the U.S. have required 10 to 15 years for construction and their costs have often escalated substantially. Moreover, because of the long lead times, planning to meet future needs has been very difficult. With the FC, smaller units of a standardized modular construction can be added to the grid in a short period of time without sacrificing efficiency. This fact greatly reduces utility financing problems and thus directly improves the financial well-being of the rate payer, who now will only pay for the amount of generation equipment actually needed by his utility. As already noted, because of the high FC efficiency, the cost of electricity is expected to be less than that for competing systems, regardless of FC system size.

Because FCs can be made in a variety of sizes, they may be placed at different locations on the grid system, thus allowing the utilities, in some instances, to reduce transmission costs. This advantage is particularly important in congested urban centers, where needed transmission and distribution facilities are expensive to install. Since FC systems operate efficiently at part load, their use may be tailored to actual requirements. Furthermore, FC systems are environmentally highly acceptable. Acid emissions and the resulting air pollution are reduced by several orders of magnitude when compared with conventional fossil-fuel-fired generators. Because of this desirable property, FCs may be located anywhere.

The siting advantages provide the opportunity to locate FCs near points of use and therefore, allow utilization of the waste heat produced by the FCs for such desirable purposes as space heating, water heating or absorption cooling. This feature has now resulted in considerable interest by U.S. gas utilities and consideration of the use of FCs in conjunction with their extensive gas-distribution systems. The combined use of electricity and heat may result in fuel-utilization systems with overall energy efficiencies of 90%. Further point-of-use FC systems are also attractive for industrial cogeneration.

Estimates made of the cost of electricity suggest that natural-gas-fuelled FC systems could produce electricity for about 6 c/kW(e)h in the US, which equals about half of the interest costs alone for many new nuclear plants.

1.1 Projected Potential

The Advanced Fuel Cell Working Group (AFCWG) was set up by the U.S. Dept.of Energy with a view to evaluating the current status of fuel cells and to identify long-range research areas that may have a significant impact on commercialisation. The AFCWG has identified five prospective fuel cell technologies, namely Phosphoric Acid Fuel Cells (PAFCs), Molten Carbonate Fuel Cells (MCFCs), Solid Polymer Electrolyte Fuel Cells (SPEFCs), Alkaline Fuel Cells (AFCs), and High Temperature Solid-Oxide Fuel Cells (SOFCs) for possible development and commercialisation in the U.S. Among these PAFCs are seen to be within a few years of commercialisation for both utility and on-site applications, whereas MCFCs and SOFCs could become available 7 to 9 years later. Commercial applications of AFCs and SPEFCs could follow PAFCs by about 10-14 years.

A desirable level of basic supporting research for FCs is estimated by the AFCWG to be about 10% of the total R&D effort after development work begins. Prior to initiation of development for commercialisation a critical level of effort must be supported that will depend on FC type and on the perceived urgency for introducing an alternative or complimentary technology into the market.

A brief discussion on the commercialisation potential and some specific areas for supporting research of each of the five types of FCs is given below.

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2. PHOSPHORIC ACID FUEL CELLS

The phosphoric acid fuel cell (PAFC) is the most mature FC in terms of technological advancement and readiness for commercialization in near- and medium-term applications. Current Acid FCs use phosphoric acid (PA) as electrolyte with relatively clean, reformed fuels such as light distillates, LPG, NG, etc. PAFCs have been under development for about 20 years. The PAFC offers potential for development as the most viable acid FC type because of its superior and unique stability characteristics and in spite of its inherently poor ionic properties. The major driving force for its dominant position has been the widespread view in the U.S. that it alone among the lower temperature FCs shows relative tolerance for reformed hydrocarbon (HC) fuels (steam raised in the FC is used for reforming, CO is removed by a shift reaction, and rejection of CO_2 occurs naturally by acid).

Significant improvements in the performance, cost, and durability of PAFCs have been realized during their development. The promise of continued improvement with important commercial implications exists to this day. Improvements have involved all aspects of PAFC development, from basic electrochemistry to overall system optimization. Crucial accomplishments in the emergence of PAFCs as a commercially acceptable power system have involved the qualification and exploitation of carbon materials as the backbone of the fuel-cell stack, reduction of electrocatalyst platinum (Pt) loadings by more than an order of magnitude with the substitution of highly-dispersed, carbon-supported catalysts for the Pt-black types used previously, and elevation of the operating temperature by 60-80 C to about 200 C, which has resulted in significant augmentation of cell and overall system efficiencies. For larger PAFCs of the type directed towards electric utility applications, the development of pressurized systems has further improved efficiency and, hence, economic attractiveness.

2.1 Initial Commercialisation

Two applications envisaged for the inital commercialization effort are: (1) a dispersed power plant, in sizes of ~7.5 - 11 MW AC, initially using reformed HCs but ultimately operating on clean coal gas (perhaps in larger units) and (2), an on-site cogeneration plant of about 0.2 MW AC that is intended for the supply of electricity from reformed NG to commercial premises, apartments, or utility buildings, with FC waste energy used for water and space heating, absorption air-conditioning cycles, etc. These are the only major market segments that have so far been identified for cost-effective technology use of current PAFCs in mature volume production. In each sector, market penetration will be determined by the usual market-place considerations: final product cost compared with costs for competing technologies.

PAFCs are now projected to establish a significant niche in the electric- and gas-utility markets and other application areas by providing benefits in terms of fuel savings, environmental impacts, and packaging and siting logistics. However, the total market penetration for PAFCs will be dictated by hard economic

decisions, and further technological advances are likely to have a major effect on the economic attractiveness of PAFC relative to available competing systems. For electric utility application, it has been estimated at EPRI that an FC efficiency improvement of 10% will increase market penetration from about 6-7% to about 16%. Efficiency improvements of this magnitude have actually been achieved during the past 3-4 years. These technological advancements will also solidify the markets reached with PAFCs during the early years of sales, while costs reflect a condition far up on the technology-learning curve. This period of time is of critical importance in establishing commercial viability for PAFCs. It could perhaps also be crucial to the sustained development effort of next-generation FCs if these show promise of operating at higher efficiencies than PAFCs.

2.2 Supporting Research

Despite the specified significant advances in PAFC technology, incentives for ongoing research and further improvements are required. There are substantial reasons to identify research areas with significant potential impact.

For instance, improvement in cathode-catalyst activity will lead to increased cell efficiency, without negatively impacting the remaining FC system in any way. At issue are inherently poor electrode kinetics at the PAFC cathode and the lack of understanding of the oxygen-reduction mechanisms that determine the efficiency of this process. Some Pt-alloy catalysts have recently yielded significantly improved cathode activity over that of Pt-only catalysts, but there is no consensus on the mechanisms that cause the changes. The significance of this work is a substantial reduction in cathode overpotential, which is large ($\sim$0.4V) and the dominant source of voltage loss. Studies to elucidate the nature of the oxygen-reduction mechanism should continue to be encouraged, together with novel catalyst systems, including transition-metal macrocycles. Systems which eliminate the need for precious metals are desirable, but only if they offer substantially equivalent performance while reducing net costs. For the anode, catalyst systems are needed with greatly improved tolerance to carbon monoxide (CO) and sulphur (S) compounds.

Similarly the long-term stability of the carbon-based catalyst-support material used in PAFCs at current cathode potentials, temperatures, and pressures is a matter of concern. A significant improvement in cell efficiency resulting from higher cathode activity will exacerbate this problem, as will improvements resulting from operations at increased temperatures or pressures. Consequently parellel research may have to be pursued to develop improved cathode-support materials.

Although phosphoric acid (PA) has clearly been the acid electrolyte of choice because it has acceptable stability, volatility, compatibility, and capillary properties, its electrode kinetics properties are poor. Studies with fluorinated sulphonic acid electrolytes have demonstrated substantially improved electrode kinetic activity over that exhibited by PA

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The potential improvements are of the same order as those sought by developing advanced cathode catalysts. However, no acceptable alternative electrolytes have thus far been found that offer significant improvements while retaining the other requisite electrolyte properties.

Some synthetic acid systems seem to have been identified now as having promise of showing superior electrode kinetic properties with acceptable stability characteristics; the latter are presumed to exist because of structural analogies with PA. These and other potentially superior acid systems must also receive attention for the purpose of developing improved acid cells.

As for electrode structures, current PAFC technology employs a teflon-bonded catalyst layer, which allows catalyst particles to be wetted by the electrolyte while sustaining gas-filled macropores for internal transport of reactant species. Mathematical modelling of catalyst-layer function suggests that, under typical cell-operating conditions, a large fraction of the active-metal crystallites may be underutilized. Although there have been some tentative indications that geometrical alterations can at least temporarily improve performance, the potential for significant improvements appears to lie with materials alterations. For example, bifunctional polymers incorporated into the electrode structure can be visualized as being both wetproofing and electron-conducting agents; similarly, proton-conducting polymers can be employed in a dual-electrolyte configuration. These modifications would affect the nature and the intimacy of the catalyst/electrolyte/wetproofing-agent morphology and interactions, with the potential for significant improvements in catalyst utilization and, hence, efficiency. Approaches to promising new materials for electrode structure, as selected on the basis of supportive modelling studies, are to be supported in an advanced R&D programme.

An important programme need is a usable theoretical approach to the theory of the distribution of electrochemical activity in porous electrodes, with special reference to the relations between such activity and the detailed structuring of pores. The aim of this work should be the formation of practical design equations.

Since the earliest FC developments, it has been recognized that a direct HC anode (i.e., one not requiring external reforming of the fuel) would be very attractive because it would improve system efficiency, reduce system cost, and reduce size. However, in order for these features to be realized, it is necessary that FC anode performance is not substantially inferior to anode performance with reformed fuel. Unfortunately, there has been little success to date in this development effort. Most of the past work has focused on methanol as fuel, and the potentials at realistic current densities have been at least 100-200 mV lower than that needed to compete effectively with indirect HC systems. Nevertheless, the potential attractiveness of direct oxidation remains as a strong incentive for further research.

3. ALKALINE FUEL CELLS

Alkaline fuel cell (AFC) technology was developed in the early 1960s for the NASA space programme. The development of AFCs for terrestrial uses is less advanced than that of PAFCs and the high-temperature FC systems because of electrolyte sensitivity to CO_2. There has recently been only a very small effort on AFCs in the US and Japan and limited work in Europe; however, terrestrial applications of AFCs lag a decade or more behind PAFCs. AFCs should properly be viewed as an alternative and complementary system that is near the beginning of the FC development cycle.

AFCs are particularly suitable for direct use with pristine H_2, since no special equipment for CO_2 removal is needed. Pure H_2 may be obtained from hydroelectric resources or nuclear electricity. Pure H_2 may also be obtained from the steam-iron process (using coal or biomass to reduce the ferric oxide) and from other coal-based technologies. The cost of H_2 from this source is unlikely to be significantly greater than that of synthetic NG.

AFCs have a few specific advantages: (1) Their cell life may ultimately be longer than that of PAFCs because of greater compatibility of alkaline electrolytes with practical cell materials. (2) Thermo-dynamic considerations show that the range of possible catalysts is greater. (3) They can operate at significantly higher efficiencies (upto 60% based on HHV) on pure H_2 than present acid cells (50% on pure H_2). (4) The cell-component cost per m^2 of AFCs are substantially lower than for PAFCs.

3.1 Transportation Applications

AFCs offer the potential of use as fuel in transportation. However, operation of AFCs for transportation, may be a vast economic undertaking and is likely to take over 20 years of developmental efforts. Nevertheless, use of AFCs in transportation is likely to have several positive effects in the long run as shown in the table I.

Table I

Advantages and disadvantages of electrochemical and chemical energy conversion in automotive transporation.

Electrochemical Systems		Chemical Systems	
Negative	Positive	Negative	Positive
Low power/wt ratio	a large increase in efficiency results	cause pollution	high power/wt ratio
present costs, without mass production, are greater than that for chemical engines in mass production	compatible with future	cause CO_2 increase in the atmosphere and perhaps a significant sea-level rise rise by 2060	
	no pollution, including CO_2 emission	vibration causes low vehicle life (5-10 y)	
	low noise	the use of a complex mechanism results in a higher frequency of repair than would probably be required for electric motors.	
	Energy-regenerative		
	better acceleration than IC engines from 0-35 mph		
	absence of vibration and perhaps longer life than better-driven commercial vehicles, which usually last 20 years		
	electric motors used in railway traction have maintenance intervals of ~10^6 miles		

The H_2 -powered AFC should be useful for future transportation because it is efficient, may well be made less costly once mass produced, and requires no noble metal catalysts with limited future availability. Development of a cheap, bipolar, non-circulating electrolyte AFC will however be required.

A thorough examination of optimal AFC and H_2 -storage system combinations for vehicles has been carried out by computer data simulation, assuming conversion efficiency to be 45%. Hydrogen storage as liquid ammonia was considered to be the most effective method.

High energy efficiency achieved with FCs will be an incentive for their future use as automotive power plants. Any major penetration into the transportation market however,requires elimination of Pt-group metals as electrocatalysts. Nevertheless AFCs offer the best prospects among the low-temperature FC systems of finding substitutes for noble metals.

3.2 Supporting Research

A few priority research areas that need to be pursued in order to render AFCs as a viable option for transportation have been identified by the AFCWG. The most important of these is the need to identify alternative electrocatalysts.

Work needs to be done to find non-noble metals and their alloys, single and mixed metal oxides, macrocycles, perhaps bio-oriented catalysts, and catalysts for peroxide decomposition. These studies should include examination of carbonate-bicarbonate-hydrate metals and solid polymer electrolytes. The studies should be aimed at finding systems that reject CO_2 and H_2O and systems with lower pH, which provide better tolerance for catalysts such as macrocycles that have long-term stability in electrolytes with pH $\simeq$ 10. Finally, systems should be sought which have acceptable stability for operations at temperatures somewhat higher than 80 ° C. These studies should include examinations of systems to remove CO_2 from CO_2 -H_2 mixtures.

Kinetic and mechanistic studies aimed at finding materials to catalyze O_2 reduction, are required mainly via a 4-electron path and with particular stress on the important characteristic of lowering the Tafel slope, in addition to increasing the exchange-current density. Good performance is sought, as a function of time, under conditions of continuous and intermittent operation. Studies are also needed of synergistic catalyst-support effects.

Further, understanding of presently-used electrode structures is needed and innovations are required to improve the performance of these structures. Studies on the wetting properties leading to optimization of electrolyte distribution are also required. Electrode modelling should be done and directed at the development of design equations.

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As regards materials research, stability of cell materials is one of the main limitations of present AFCs. For instance, cell lifetimes must be extended to 40,000 h. Further, work to obtain modified, doped carbons with improved characteristics are also required. New materials such as electronic conducting polymers may be considered, particularly for bipolar cell types. On the other hand, improvements in cell design should be aimed at development of bipolar systems, minimization of ohmic losses, heat and water management, and evaluation of circulatory electrolyte systems.

Generally, new, low-cost, and stable supports are needed for the more expensive catalysts; instead, carbons, carbides, nitrides, borides, and oxides can be tested as catalyst supports.

Because of the stress laid on the difficulty of removing CO_2 from mixtures arising from the reforming of HCs, the use of AFCs has often been associated with the availability, on a massive scale, of pure H_2 . This fuel may become available in the future from the use of nuclear electricity in off-peak periods or from hydroelectric power, as at present in Canada, or, according to Japanese predictions, in 4-8 years from solar cells. In view of these possibilities, continued work on hydrogen storage is recommended; without H_2 , AFCs may not be practical. Liquid NH_3 is the first among possible hydrogen-containing fuels for transportation applications with AFCs.

4. SOLID POLYMER ELECTROLYTE FUEL CELLS

The SPEFC was the first FC system to find practical application when it was used as the non-propulsive power plant for the manned Gemini terrestrial-orbit missions in 1963-65. Since then, the SPEFC has been substantially refined, particularly with respect to membrane reliability and power density. A series of improvements using materials like teflon, polystyrene sulphuric acid were being introduced. From the early 1970s onwards the fully fluorinate Nafion[R] membrane, which is chemically and electrochemically stable to more than 200°C, became available from DuPont. This material removed the stability constraints of the earlier membranes and allowed operation at temperatures up to about 100°C. The temperature constraint is set by dehydration of the membrane above this temperature and the resultant loss of ionic conductivity. In addition, the Nafion[R] film affords a lower intrinsic oxygen-reduction overpotential on platinum than the earlier electrolytes, which results in performance improvements under all temperature conditions. Together with progressive improvements in cathode structure, the FC performance at 80°C was about 50 mV better than that of a PAFC at 190°C operating at the same current density on pure H_2 . However, state-of-the-art catalyst loading in the SPEFC system is far higher than in the PAFC system.

The present design has been developed by the General Electric Company for terrestrial applications and has advantageous features such as: relative simplicity, CO_2 rejection, and moderately high cell voltages at acceptable power densities.

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Nevertheless, this system presently exhibits some shortcomings which render terrestrial non-military applications impractical: (a) high cost of the polymer membrane electrolyte ($400/m^2 or $200/kW); (b) high Pt loadings for the cathode and anode (the combined loading is 8 mg/cm^2 or $\approx$ $450/kW for the catalyst alone); (c) satisfactory operation only on H$_2$ with very low CO content (1 ppm); (d) relatively low operating temperatures ($\leq$ 100 C), which severely restrict the use of cell heat for fuel processing to produce H$_2$.

4.1 Manifold Use

The SPEFC system may be competitive with the PAFC for electric utility, dispersed-power-plant applications and, provided catalysts other than noble metals are found, is superior for vehicular applications, including the personal transportation vehicle. However, the SPEFC system as a whole is probably about a decade behind the PAFC in its development for commercial use. Nevertheless, the potential transportation application justifies long-range research in support of this FC system.

4.2 Research Priorities

Long-range research areas include development of new and modified cation-exchange membranes (proton conductors) offering the promise of lower cost and operation at temperatures $\approx$ 150° C, with reasonable conductivities and affording reasonable kinetics for cathodic and anodic reactions with available electrocatalysts. This research should include the synthesis of new membrane materials and their electrochemical evaluation. A relatively large industrial effort is already in progress to find new, lower-cost membranes for the chlor-alkali industry and other applications. This work may become a source of promising new membrane structures for the SPEFC. Careful electrochemical evaluation will be necessary under conditions that are suitable for use in advanced SPEFCs.

For stability reasons, the most promising new polymeric materials are likely to involve fluorinated organic structures. Inorganic proton conductors can also be considered for the purpose. Specific types of materials, which are possible candidates for electrolytes, include: (a) fluorinated organic proton-conducting polymers with alternative acid groups to the presently used sulphonic acids (e.g., phosphoric, phosphonic, phosphinic, silicic acids); (b) Nafion-type membranes (sulphonic acid groups), impregnated with very concentrated ($\sim$85%) phosphoric acid or other highly conducting acids to suppress the vapor pressure of water in the inverse micellar structure, while still retaining sufficient conductivity and stability at temperatures $\geq$ 140°C; (c) gelled ion-exchange type proton-conducting polymeric materials; (d) gelled concentrated-acid electrolytes with adequate conductivities and stabilities at elevated temperatures (e.g. borophosphates, borofluorosulphonic acids); (e) multilayer polymeric proton-conducting membranes (e.g., polymer membranes with different anolyte, bulk and catholyte layers, optimized for low electrode polarization while retaining high conductivity and

low leakage of H_2 and O_2 between the anodes and cathodes; (f) proton-conducting inorganic solid membrane materials such as heteropolyacids (e.g., polymolybdates and tungstates), including dispersions of these in teflon and other fluorinated polymer matrices.

The inorganic materials may be capable of operation at much higher temperatures than organic polymeric materials and offer the possibility of direct oxidation of methanol and other fuels. These are an extension of the SOFC concept but involve proton conductors rather than oxide-ion conductors.

As for electrocatalysts, little information is available concerning the factors controlling the polarization of Pt-catalyzed air cathodes. These studies are necessary as a first step in achieving more effective utilization of Pt and finding effective, lower-cost alternative catalysts to Pt (e.g., oxides, transition-metal complexes including macrocycles, and non-precious metals). Some catalysts may be stable in the polymeric electrolytes, while lacking adequate stability in concentrataed phosphoric acid or KOH. This fact may make it possible to use some of the highly active macrocycles which catalyze the 4-electron reduction of O_2. Kinetic-mechanistic studies are required with these promising electrocatalysts in order to optimize them with respect to activity and long-term stability. Research on electrocatalysts for SPEFCs should include supported catalysts on various stable substrates.

Anode catalysts also pose problems similar to those of the cathode with H_2 fuel. In addition, research on electrocatalysts for the direct oxidation of methanol and other fuels should be initiated if new proposals are made on how to accomplish oxidation at reasonable potentials and current densities. Platinum is not sufficiently active at temperatures below 200°C and new ideas are needed before further research is initiated.

Similarly, relatively little research has been reported on electrode structures and the relation of transport processes to structures is not clear. It is questionable if substantial fractions of the catalysts are accessible to the chemical reactants and electrolyte, and are also in electronic contact in the present electrode structures. The electrode structures presently used in SPEFCs do not appear to be near-optimal designs. Specific research priorities include: (a) characterization of the structures of existing SPEFC electrodes; (b) studies of O_2 and H_2 transport and electrolyte access to the catalysts in existing structures, including modelling; (c) innovative development of more effective electrode structures.

If improved membranes and electrocatalysts can be realized for the SPEFC, then it would be desirable to consider innovations in overall cell design. As an example, the monolithic structure proposed for the SOFC might be applicable also to the SPEFC. It is conceivable that a monolithic, all-polymer FC can be developed with polymer anodes, polymer cathodes and polymer electrolyte. The progress of this work is clearly contingent on new and innovative ideas.